D-A096 026   BEN-GURION UNIV OF THE NEGEV BEERSHEBA (ISRAEL) DEPT --ETC F/G 20/5
              ELECTRONIC ENERGY TRANSFER FROM NITROGEN MOLECULES TO METAL ATO--ETC(U)
              NOV 80   S ROSENWAKS, I NADLER   AFOSR-78-3718
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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. Report Number AFOSR-TR-80-17	2. Govt Accession No. AD-A096 026	3. Recipient's Catalog Number Final 25, 78-31 Aug 80
4. Title (and Subtitle) Electronic Energy Transfer from Nitrogen Molecules to Metal Atoms	5. Type of Report & Period Covered Final, 78 Sept. 01 - 80 Aug. 31
	6. Performing Org. Report Number
7. Author(s) S. Rosenwaks and I. Nadler	8. Contract or Grant Number AFOSR-78-3718
9. Performing Organization Name and Address Department of Chemistry Ben-Gurion University of the Negev Beer-Sheva, Israel	10. Program Element, Project, Task Area & Work Unit Numbers 61102F 2301-B1
11. Controlling Office Name and Address European Office of Aerospace Research and Development Box 14 FPO New York 09510	12. Report Date 30 November 1980
	13. Number of Pages 18
14. Monitoring Agency Name and Address	15.

16. & 17. Distribution Statement

Approved for public release; distribution unlimited.

18. Supplementary Notes

19. Key Words

Electronic Energy Transfer, Population Inversion, Energy Pooling, Laser Induced Fluorescence.

20. Abstract

The report describes up-to-date data of a comprehensive study on the interaction of metastable nitrogen molecules with metal atoms and with other N_2 molecules in several electronic states. Emission spectra resulting from reaction of "clean" $N_2(A^3\Sigma_u^+)$ with Cu, Pb, and Sn atoms were studied using a flowing afterglow apparatus. The population distribution of the Cu atoms states show non-Boltzmann distribution and population inversion between some of the states. The electronic energy transfer rate constant from $N_2(A)$ to Cu was found to be of the order of 1×10^{-10} cm³ molec⁻¹ sec⁻¹. Laser induced fluorescence technique was used to monitor the $N_2(B^3\Pi_g, v'=0)$ decay in the presence of Ar and N_2. A non-exponential decay indicates a distributed energy distribution among the electronic levels adjacent to $N_2(B)$. The $N_2(A)$ energy pooling reaction, which is a competitive reaction to the energy transfer from $N_2(A)$, was studied too. The Herman Infrared system (HIR), which is an unassigned N_2 band system, was found to provide a

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the energy pooling reaction. A lower limit to the formation rate constant for the upper state of the $\text{III}r$ was found to be 2.5×10^{-11} cm^3 molecules^{-1} sec^{-1}. This upper state must be below 13 eV and probably is below 12.5 eV. Currently we are engaged in an effort to produce $N_2(B)$ in a novel method using two photon absorption techniques and in measuring the overall rate constant for energy transfer from $N_2(A)$ to some metal atoms.

This report has been reviewed by the Information Office (EOARD/CI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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ELECTRONIC ENERGY TRANSFER FROM NITROGEN MOLECULES TO METAL ATOMS

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30 November 1980

Final Scientific Report, 1 September 1978 - 31 August 1980

Prepared for

Air Force Office of Scientific Research
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European Office of Aerospace Research and Development
London, England

Introduction

Electronic energy transfer (EET) from metastable species to specific energy levels of atoms and molecules is one of the best routes for obtaining population inversion. EET from metastable nitrogen molecules to metal atoms (M) is one of the interesting possible routes to populate high electronic states. Perhaps the most spectacular reactions of metastable nitrogen are those obtained in mixtures of active nitrogen with metal atoms or metallic compounds [1-3]. In many instances these reactions are accompanied by intense flames due to neutral metal atoms emission spectra. It has been proposed [2,3] that the metal atoms are excited by energy transfer from $N_2(A^3\Sigma_u^+)$. One of the main difficulties in interpreting the experimental results stems from the fact that active nitrogen contains N atoms and N_2 molecules in various energy levels which change rapidly due to reactive and radiative processes [1].

In order to clear up the difficulties we employed novel methods for production of $N_2(A)$, $N_2(B,v)$ and translationally cold ground state metal atoms in the gas phase. Along with these experiments our interest was extended to related questions where sufficient information could not be found.

Three main topics were studied in our laboratory using different experimental techniques. a) Reactions of "clean" $N_2(A)$ with Cu, Pb, and Sn atoms were studied using a flowing afterglow apparatus which is described elsewhere [4,5]. b) In a similar apparatus it was found that the $2N_2(A)$ energy pooling (EP) reaction produces along with $N_2(C^3\Pi_u)$, $N_2(C'^3\Pi_u)$,

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and $N_2(B^3\pi_g)$ also the upper state of the N_2 unassigned Herman infrared system (Hir) [6]. c) In order to measure EET from $N_2(B^3\pi_g)$ to metal atoms several methods of $N_2(B,v)$ production were tried: 1) laser excitation of $N_2(A)$ [7], 2) EET from $Xe(^3P_2)$ which is produced either in a flow apparatus [8] or by laser excitation [17]. Some of our results have already been published (see attached bibliography) and these will be reviewed briefly.
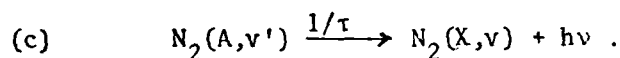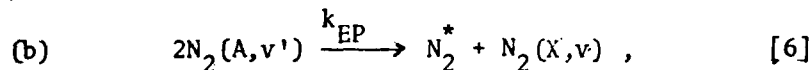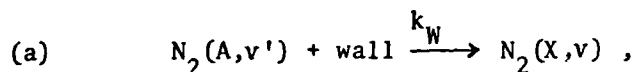
Reactions of $N_2(A^3\Sigma_u^+)$ with metal atoms

Emission spectra resulting from reactions of $N_2(A)$ with copper, lead, and tin atoms, in the gas phase, were studied. The experimental setup has been described previously [4,5]. Briefly, it consists of three main parts. a) An $N_2(A)$ generator, where N_2 is excited by energy transfer from argon metastable atoms formed in a dc discharge. b) An evaporation furnace, where metal atoms are evaporated from a resistively heated crucible. c) A calibrated detection system consisting of a monochromator, PMT, picoammeter and a strip chart recorder.

EET to both Cu and Pb exhibit visible flames. The fluorescence spectra of all three metals show populations of energy levels up to 6.13 eV. Most of the work was done with Cu and some of the results-have already been published [4,5]. The Cu population distribution indicates that the electronic energy transfer is the nearly resonant process, $N_2(A,v') + Cu(^2S_{1/2}) \rightarrow N_2(X,v) + Cu^*$, and that the transfer is most efficient for $N_2(A,v') \rightarrow N_2(X,v)$ transitions with large Franck-Condon factors. The

preferential energy transfer results in population inversion between some of the Cu states. The similarity of the population distribution of the Cu states in the $N_2(A) + Cu$ and in the $NF_3 + Cu$ systems [4,9] corroborates the suggestion [9] that in the latter case the inverted population in copper originates from $N_2(A)$ produced chemically via a chain of consecutive reactions [9,10].

In order to calculate EET rate constants from $N_2(A)$ to M, we measured the reactants concentration at several positions along the reaction flow tube. One has to obtain first the quenching of $N_2(A)$ in the absence of metal atoms:

(a) $\qquad N_2(A,v') + wall \xrightarrow{k_W} N_2(X,v)$,

(b) $\qquad 2N_2(A,v') \xrightarrow{k_{EP}} N_2^* + N_2(X,v)$, $\qquad$ [6]

(c) $\qquad N_2(A,v') \xrightarrow{1/\tau} N_2(X,v) + h\nu$.

The observed first order decay of $N_2(A)$ along the flow tube indicates that the energy pooling reaction (b) is negligible in our observation zone. Since $\tau_{N_2(A)} \cong 2$ sec, reaction (c) is negligible as well and k_W can thus be found:

(1) $\qquad [N_2(A)]_t = [N_2(A)]_0 \, \exp(-k_W t)$

where t is the time of flow from the first observation window to each of the other windows downstream. The value obtained for k_W at 1 torr $(Ar/N_2 \sim 10/1)$ was ~ 120 sec^{-1} and wall deactivation is therefore accounted for in the analysis of the results (see equation (7) below).

Cu atoms concentration in the ground state ($^2S_{\frac{1}{2}}$) is measured by means of atomic absorption technique using a Cu hollow cathode lamp. It was found experimentally that the Cu concentration, along the flow tube, obeys, approximately, the following equation:

(2) $$[Cu]_t = [Cu]_0 \, (1 - \alpha t)$$

where α is an observed constant at fixed furnace temperature and flow conditions.

Cu emission resulting from the reactions

(d) $$N_2(A,v') + Cu(^2S_{\frac{1}{2}}) \xrightarrow{\ k_i\ } Cu_i + N_2(X,v) \ ,$$

(e) $$Cu_i \xrightarrow{\ 1/\tau_i\ } Cu_j + h\nu_{ij} \ ,$$
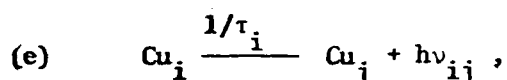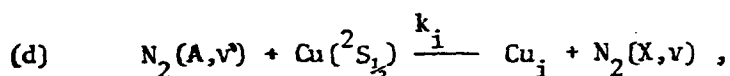
is monitored at the observation windows downstream. Using a steady state approximation for the excited Cu states (at any observation point), one obtains that the Cu emission intensity (I) is proportional to the $N_2(A)$ concentration:

(3) $$\frac{d[Cu_i]}{dt} = k_i[Cu]\,[N_2(A)] - 1/\tau_i[Cu_i] = 0 \ ,$$

also

(4) $$\frac{1}{\tau_i}\,[Cu_i] \propto (I_{ij}) \ ;$$

hence

(5) $$[N_2(A)] \propto (I_{ij})/k_i[Cu] \ .$$

The quenching rate constant of $N_2(A)$ by Cu, (k_T), can be obtained from the relation:

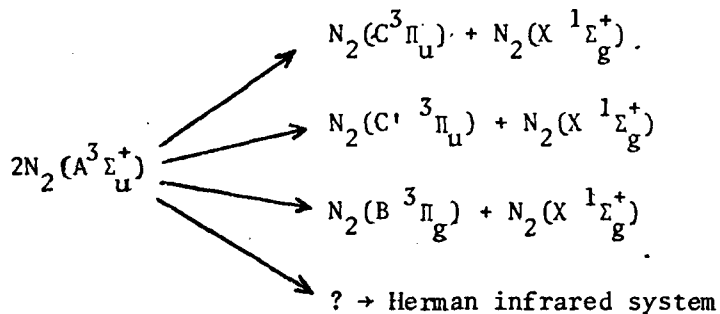(6) $$\frac{d[N_2(A)]}{dt} = - \{k_T[Cu]_0 \, (1 - \alpha t) + k_W\}[N_2(A)] \ .$$

Integrating equation (6), and substituting $[N_2(A)]$ from (5) and $[Cu]$ from (2) one gets:

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(7) $\ln\{(I_{ij})_0/(I_{ij})_t\} = \{k_T[Cu]_0(1-\alpha t/2) + k_W\}t - \ln(1-\alpha t)$..

The value of t is calculated using the measured mass flux, pressure and tube diameter, and assuming a plug flow profile (which is justified under our experimental conditions [12]). Preliminary analysis of the data, using equation (7), gives $k_T \sim 1 \times 10^{-10}$ cm^3 $molec^{-1}$ sec^{-1} [20]. An additional method is now being developed in order to cross check the measurements of the Cu atoms concentration. This method uses small plates inserted inside the flow tube in order to calculate the concentration from the weight of the Cu collected on the plates [20].

The nitrogen energy pooling reaction

The total rate constant of the $N_2(A)$ energy pooling reaction,

$$2N_2(A^3\Sigma_u^+) \nearrow \begin{array}{l} N_2(C^3\Pi_u) + N_2(X\ ^1\Sigma_g^+). \\ N_2(C'\ ^3\Pi_u) + N_2(X\ ^1\Sigma_g^+) \\ N_2(B\ ^3\Pi_g) + N_2(X\ ^1\Sigma_g^+) \\ ? \rightarrow \text{Herman infrared system} \end{array}$$

is $\sim 1.0 \times 10^{-9}$ cm^3 $molecule^{-1}sec^{-1}$ [6, 13 and references therein].

The energy pooling reaction was previously studied by monitoring the $N_2(C)$ emission [14a]; subsequent independent studies [14b,c] are in agreement on the $N_2(C)$ formation rate constant (2.5×10^{-10}). Based upon measured intensities and published values for quenching of $N_2(B)$,

Oskam et al. [14b] suggested that the $N_2(B)$ formation rate constant is 4.4 times larger than that for $N_2(C)$. Since $N_2(B)$ can be formed in several ways in a N_2 discharge and since the quenching and vibrational relaxation rate constants are somewhat uncertain, the rate constant for $N_2(B)$ formation from energy pooling is not well established. Intersystem crossing to $N_2(W^3\Delta_u)$ and other adjacent electronic levels contribute to the complexity of the $N_2(B,v)$ quenching (see the following section).

Since the energy pooling reaction of $N_2(A)$ has such a large rate constant it is a/very efficient competitive reaction to electronic energy transfer from $N_2(A)$, and might rule out $N_2(A)$ as energy storage for lasing purposes. Because of the large uncertainty in $N_2(B)$ formation we felt that a reconfirmation of this rate constant is worthwhile.

In our experiment [6], molecular N_2 emission, observed from an $Ar(^3P_{0,2})$ and $Xe(^3P_2)$ + N_2 flowing afterglow apparatus, indicates that the energy pooling reaction generates the emission from the Herman infrared system which is an unassigned N_2 band system. A lower limit to the formation rate constant for the upper state of the Herman infrared system was found to be 2.5×10^{-11} $cm^3 \cdot sec^{-1}$ molecule^{-1}. This upper state must be below 13 eV and probably is below 12.5 eV above ground state [4]. The $2N_2(A)$ EP reaction also forms $N_2(B^3\Pi_g, v \geqslant 8)$ but a rate constant cannot be assigned from the present data.

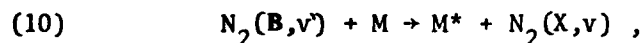$N_2(B^3\Pi_g, v)$ formation and quenching

Under our experimental conditions $N_2(B,v)$ molecules might suffer several collisions during their fairly long radiative life time, 4-10 μsec [15]. Hence they might be a source of EET to metal atoms when they are produced in the presence of metal atoms or metalic compounds. $N_2(B)$ is known to be formed in many reactions, e.g., electrical discharge in nitrogen [1a], energy transfer from metastable rare gas atoms [8], and chemical production via a chain of consecutive reactions resulting from NF_3 + M reaction [9]. The motivation to the present work arose from our previous results on the NF_3 + M reaction, where the N_2 first positive band, $N_2(B) \rightarrow N_2(A)$, was observed. Qunatitative kinetic study could not be done in this system due to the presence of other excited and reactive species.
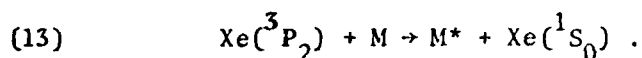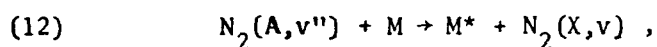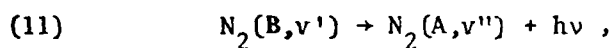
Since $N_2(B)$ radiates to the long lived $N_2(A)$ state it is obvious that any source of $N_2(B)$ for EET experiments includes $N_2(A)$ molecules as well. Therefore, a preliminary study on the EET from $N_2(A)$ has been essential.

Several methods of $N_2(B,v)$ production were tried. In the reaction

$$(9) . \quad Xe(^3P_2) + N_2(X,v=0) \rightarrow Xe(^1S_0) + N_2(B,v=2-5) \ ,$$
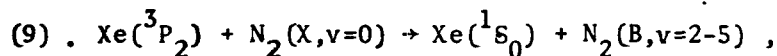
v = 5 is populated more than the other vibrational states [8]. When a flow of N_2 + M is mixed with $Xe(^3P_2)$, additional reactions can take place:

$$(10) \qquad N_2(B,v') + M \rightarrow M^* + N_2(X,v) \ ,$$

(11) $N_2(B,v') \rightarrow N_2(A,v'') + h\nu$,

(12) $N_2(A,v'') + M \rightarrow M^* + N_2(X,v)$,

(13) $Xe(^3P_2) + M \rightarrow M^* + Xe(^1S_0)$.

In order that reaction (10) will be significant one has to increase the
metal atoms concentration, otherwise reaction (11) will lead to EET
mainly through reaction (12). Metal concentration increment will increase
reaction (13) as well. In experiments with $M = Hg$ either reactions (13)
or (9) $\rightarrow$ (11) $\rightarrow$ (12) were the main processes.* Since rate constants for
quenching of $Xe(^3P_2)$ by metal atoms are not reported, but have been
recently suspected to be large for Cu [16], such a system is not suitable
for $N_2(B)$-Cu EET reactions.

An attempt to produce a pulsed source of $Xe(^3P_2)$ via two photon
absorption of the KrF laser emission [17] failed, probably due to three
photon ionization processes which compete with the two photon process [18].

$N_2(B^3\Pi_g,v)$ states were also produced by laser excitation of
$N_2(A^3\Sigma_u^+,v)$ in Ar carrier gas in a flowing afterglow apparatus [19].
The experimental setup is presented in Fig. 1. $N_2(A,v')$ molecules were
produced in the previously described flowing afterglow system [4,8] where

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*We chose Hg since preliminary results showed slow EET from $Xe(^3P_2)$
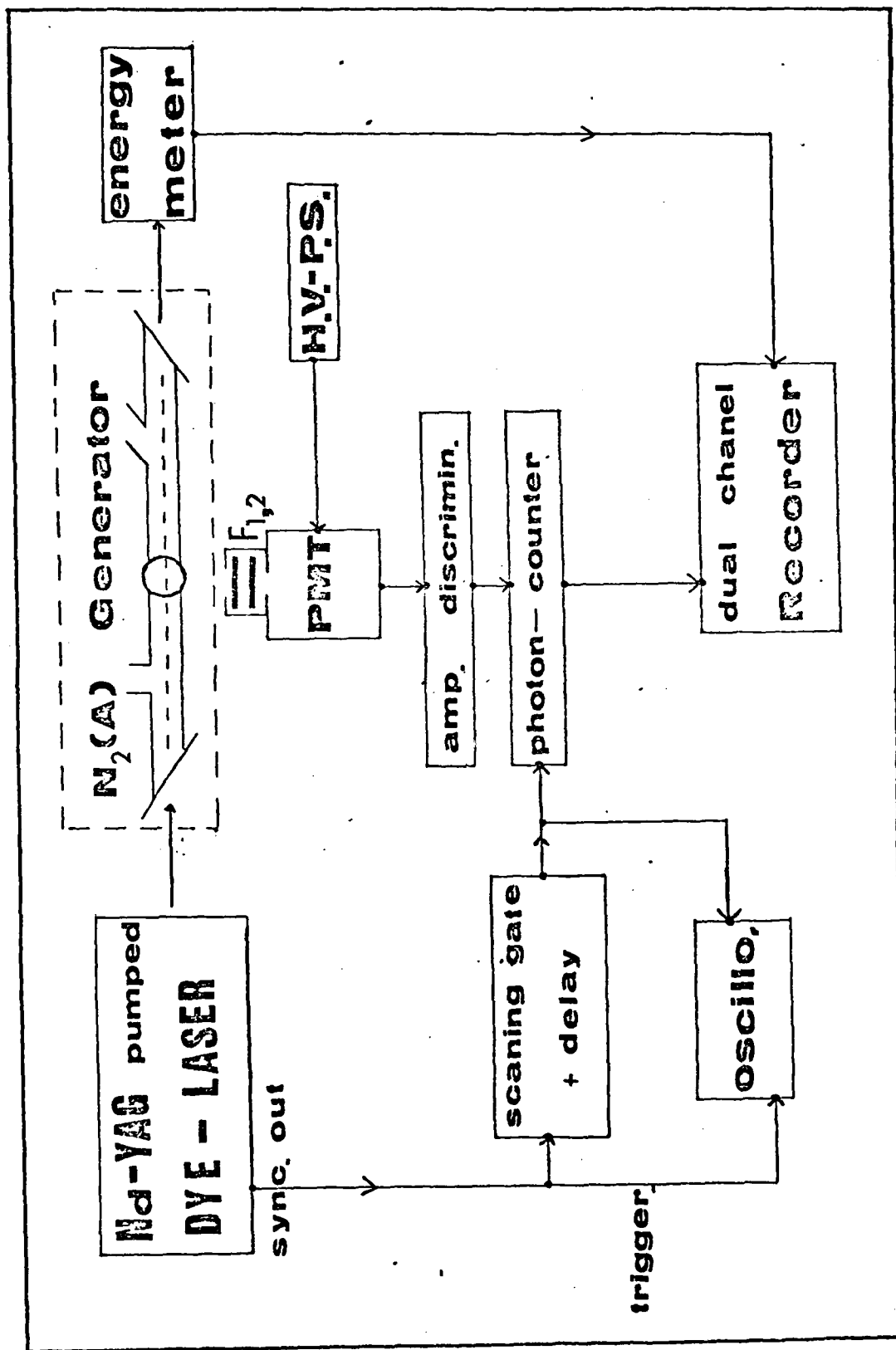to Hg at room temperature [18].

Figure 1

Schematic of the experimental setup of the $N_2(A) \xrightarrow{LASER} N_2(B,v) \xrightarrow{Fluorescence} N_2(A)$ LIF experiment. A Quanta-Ray laser emission excites $N_2(A)$ molecules produced in a flowing afterglow apparatus. The focused fluorescence passes through/cut-on filter (F_1) and interference filter (F_2). The time resolved spectra is monitored by a gated photon counter.

baffle arms with Brewster angle windows were added. The operating pressure range of our apparatus was 0.7-10 torr. Using a Nd-YAG pumped dye laser (Quanta-Ray DCR-1, PDL system), with rhodamine-590, rhodamine-640, and oxazine-720, we generated $N_2(B,v=3-9)$, pumping $N_2(A,v=0-4)$ in $\Delta v = 3,4,5$ transitions. The $N_2(A,v\geqslant 2)$ population is heavily relaxed when N_2 pressure rises above 0.2 torr [14], so it was hard to populate $N_2(B,v\geqslant 10)$. Experiments of $N_2(B,v=0-2)$ production, using an IR tunable laser source, are in progress.

The fluorescence was focused by a cylindrical lens on a R-928 Hamamtsu PMT, passing through a cut-on filter and an interference filter (typically 10 nm FWHM). By carefully choosing the interference filter and tilting it we eliminated the possibility of detecting simultaneously two $N_2(B)$ vibrational levels emission. The PMT signal was amplified and monitored by a PAR 1109/1120 photon counting system driven by a scanning gate to produce the time resolved fluorescence emission. Two typical decay curves are presented in Fig. 2. All vibrational levels initially populated by the laser, v=3-9, showed double exponential decay. The initial fast decay is associated with collisional coupling of $N_2(B,v)$ level to adjacent energy levels (see Fig. 3). The slow decay represents the overall decay of these coupled levels. The decay curves show that relaxation of $N_2(B,v)$ is significant at pressures of Ar in the torr range, and of N_2 in the mtorr range. Our data suggest that under the present experimental conditions the chemistry of $N_2(B)$ must consist also of contributions from adjacent states. This suggestion may significantly affect existing interpretations [11]
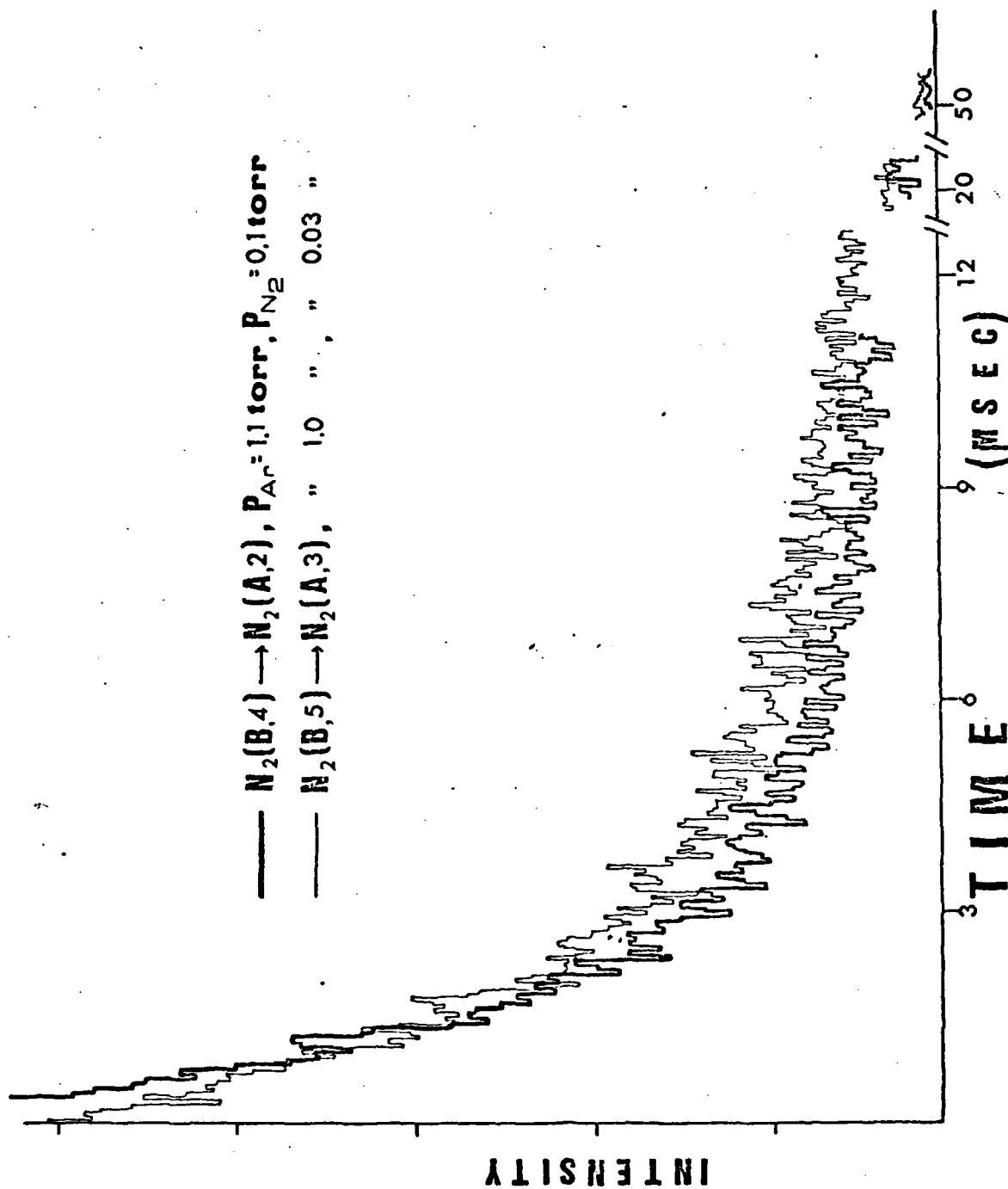
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Figure 2

Typical decay plots present a multiexponential decay which is interpreted as fast collisional
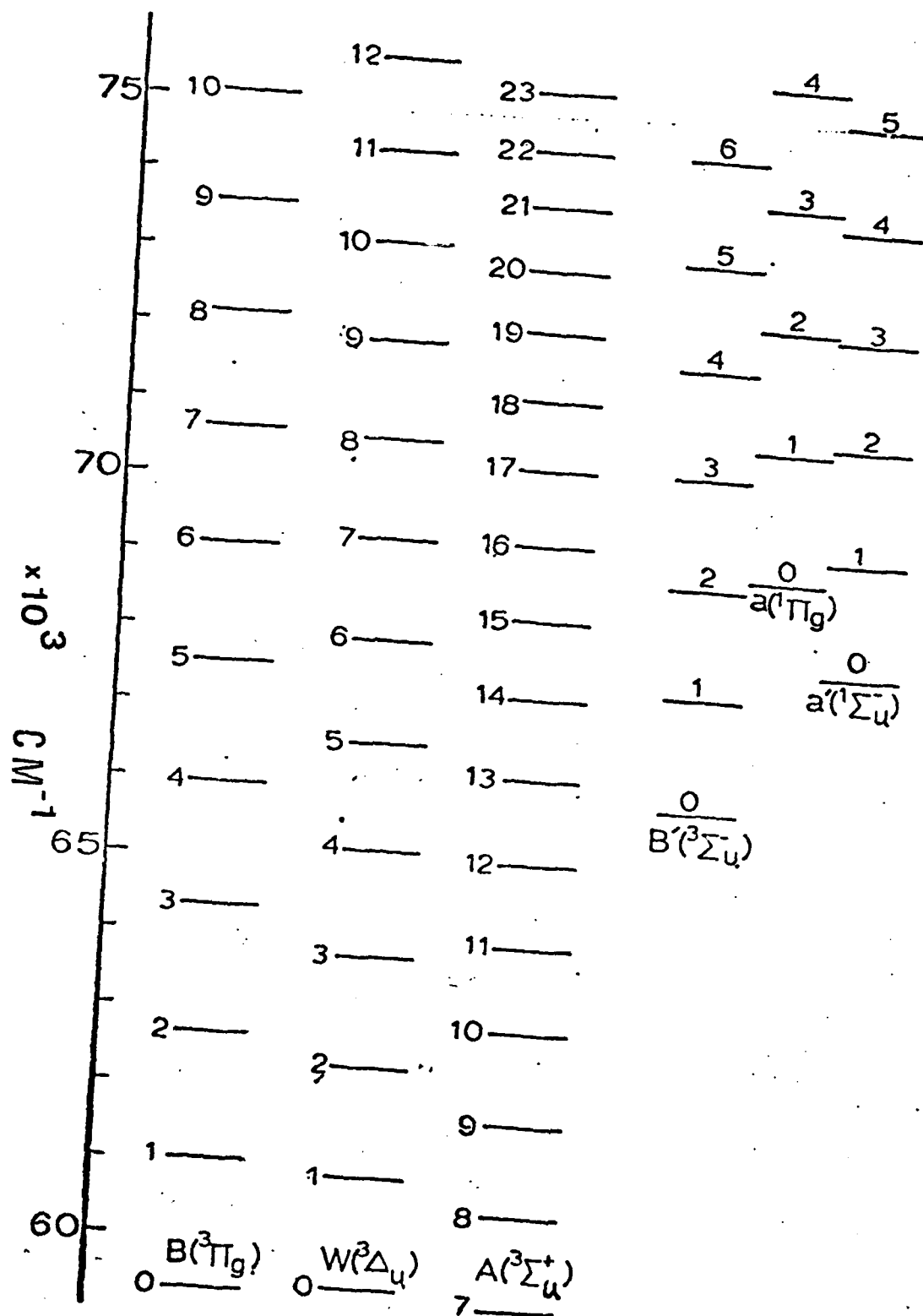coupling of $N_2(B,v)$ to adjacent energy levels and slower overall decay of these coupled levels.

Figure 3

N_2 energy levels in the 59000-76000 cm^{-1} energy range.

which have been made assuming that only $N_2(B)$ was present and might explain the discrepancies between different published $N_2(B,v)$ radiative lifetimes [7]. At the very least many claims about "initial" $N_2(B)$ vibrational population from a given excitation source need revisions because of the very fast vibrational relaxation. A comprehensive study on $N_2(B,v)$ relaxation and energy redistribution, in Ar and N_2 buffer gases, using a high resolution monochromator, a Biomation 6500 waveform recorder and an on-line computer is in progress. Preliminary results show fast building of $N_2(B)$ v-1, v-2, and v-3 when pumping $N_2(A)$ to $N_2(B,v)$. A method of $N_2(B^3\Pi_g,v)$ production by two photon absorption from $N_2(X\ ^1\Sigma_g^+, v=0)$ is now being studied. Such a method, if successful, will allow EET measurements from $N_2(B)$.

Conclusion

The results of this research show that electronic excitation of metal atoms by $N_2(A)$ molecules is easily obtained in the metals studied. Moreover, EET is a fast and preferential process resulting in population inversion between some of the Cu states. Evidence is presented for the possible importance of the Franck-Condon principle in the collisional quenching of $N_2(A)$ by Cu. The similarity of the population distribution of the Cu states in the $N_2(A)$ + Cu and in the NF_3 + Cu systems corroborates the suggestion that in the latter case the inverted population in copper originates from chemically produced $N_2(A)$.

LIF studies of $N_2(B,v)$ have demonstrated a multiexponential decay which is interpreted as a fast collisional coupling of $N_2(B,v)$ to adjacent

energy levels and a slower overall decay of these coupled levels. Our
results may have bearing on existing interpretations of $N_2(B)$ chemistry.
The $2N_2(A)$ energy pooling rate constant could be estimated more
accurately once the $N_2(B,v)$ quenching rate constant are found [13].
This accuracy is needed since the energy pooling reaction is a competitive
reaction to EET from $N_2(A)$. The information presented on the N_2
Herman infrared system due to energy pooling may help in the identification
of the upper and lower states of this unassigned band.

Acknowledgment

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5. A. Rotem, I. Nadler and S. Rosenwaks - "Laser Induced Fluorescence Studies of $N_2(B^3\Pi_g)$", to be published.